REPORT DOCUMENTATION PAGE

Form Approved
OMB No. 0704-0188

1. REPORT DATE *(DD-MM-YYYY)*	**2. REPORT TYPE** Technical Paper	**3. DATES COVERED** *(From - To)*
4. TITLE AND SUBTITLE		**5a. CONTRACT NUMBER**
		5b. GRANT NUMBER
		5c. PROGRAM ELEMENT NUMBER
6. AUTHOR(S)		**5d. PROJECT NUMBER** 2303
		5e. TASK NUMBER M1A3
		5f. WORK UNIT NUMBER 346127
7. PERFORMING ORGANIZATION NAME(S) AND ADDRESS(ES)		**8. PERFORMING ORGANIZATION REPORT**
9. SPONSORING / MONITORING AGENCY NAME(S) AND ADDRESS(ES) Air Force Research Laboratory (AFMC) AFRL/PRS 5 Pollux Drive Edwards AFB CA 93524-7048		**10. SPONSOR/MONITOR'S ACRONYM(S)** **11. SPONSOR/MONITOR'S NUMBER(S)**

12. DISTRIBUTION / AVAILABILITY STATEMENT

Approved for public release; distribution unlimited.

13. SUPPLEMENTARY NOTES

14. ABSTRACT

20030127 205

15. SUBJECT TERMS

16. SECURITY CLASSIFICATION OF:			**17. LIMITATION OF ABSTRACT**	**18. NUMBER OF PAGES**	**19a. NAME OF RESPONSIBLE PERSON** Leilani Richardson
a. REPORT Unclassified	**b. ABSTRACT** Unclassified	**c. THIS PAGE** Unclassified	A		**19b. TELEPHONE NUMBER** *(include area code)* (661) 275-5015

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2303M1 #3

MEMORANDUM FOR PRS (In-House Publication)

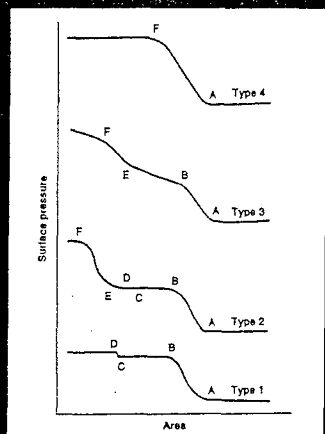
FROM: PROI (STINFO) 31 Oct 2001

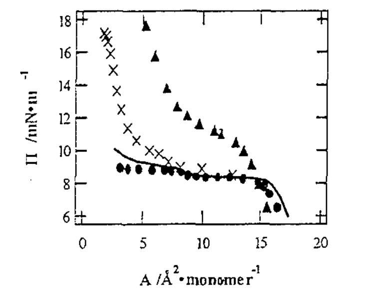
SUBJECT: Authorization for Release of Technical Information, Control Number: **AFRL-PR-ED-TP-2001-218**
Brent D. Viers, et al., "Basic and Applied Research on Hybrid Organic/Inorganic Materials for Propulsion and Space"

American Chem Soc Wkshp: Org/Inorg Hybrids **(Statement A)**
(Napa, CA, 17-20 November 2001) (DEADLINE: 16 Nov 01)

PDMS Langmuir Blodgett Analysis

- Inherent dimensionality effects



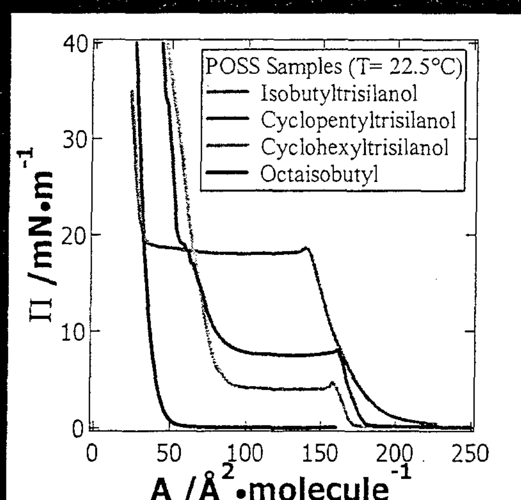


PDMS terminated with ▲ di COOH;
× mono COOH; ● di $Si(CH_3)_3$; — di OH

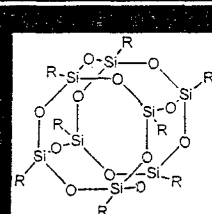
- Highly sensitive to functionality

Lenk, Koberstein, et. Al. *Langmuir*, **10**, 1857, (1994)

Results – P-A Isotherms of POSS Samples

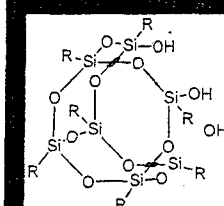


R_8T_8



Weak Interactions

R_7T_7

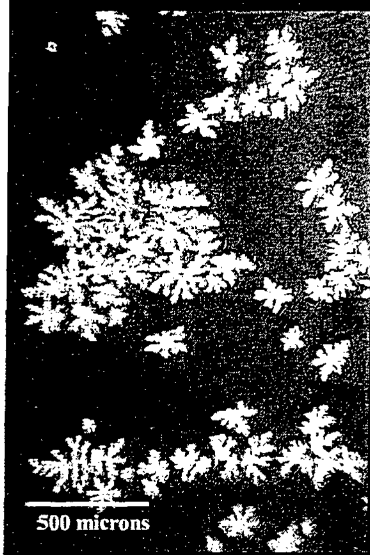


Stronger Interactions

Virginia Tech

DISTRIBUTION STATEMENT A
Approved for Public Release
Distribution Unlimited

Results – BAM of Isobutyltrisilanol-POSS

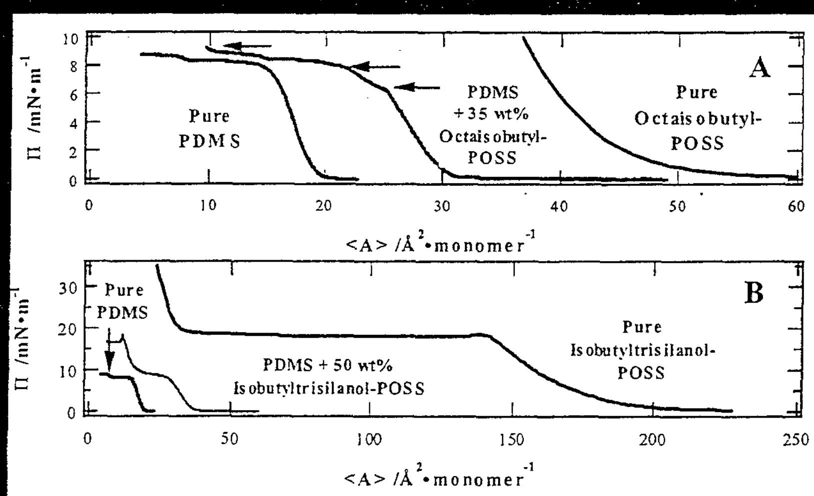


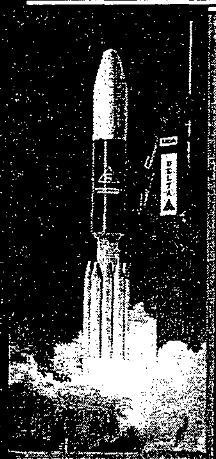
- Non-equilibrium phase transition induced by pressure
- Supersaturation results in non-equilibrium 2-D dendritic growth of the more condensed phase
- Pressure relaxation drives the system to the equilibrium state characterized by round domains
- Observed in a few other surfactant systems*

*Iimora,K.-I.; *et al. Langmuir* **2001**, *17*, 4602

POSS-PDMS Blends

$$\Delta G^{*,\sigma} = \int_{\Pi}^{\Pi^*} (A_{12} - x_1 A_1 - x_2 A_2) d\Pi$$





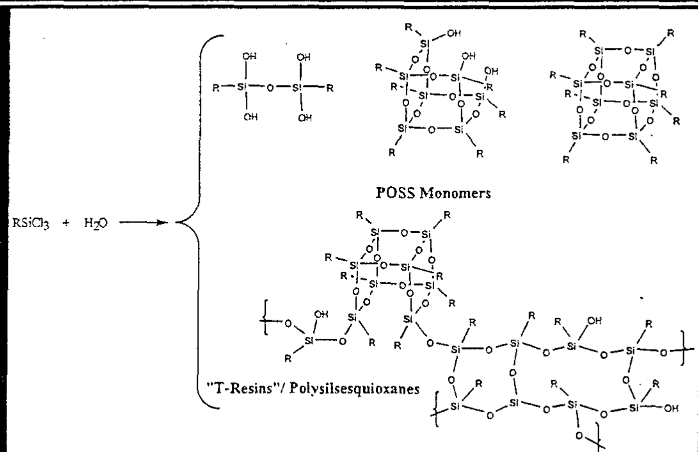
Basic and Applied Research on Hybrid Organic/Inorganic Materials for Propulsion and Space

POSS is NOT just the smallest silica

Dr. Brent D. Viers
Propulsion Sciences Division
Edwards Air Force Research Lab

Dr. Shawn H. Phillips, Dr. Timothy S. Haddad, Dr. Rusty Blanski, Maj. Steve Svejda Ph.D., Prof. Andre Y. Lee, Justin Leland, Pat Ruth, Brian Moore, Capt. Rene Gonzalez, , Prof. Patrick T. Mather, Prof. Frank Feher, Prof. Benjamin S. Hsiao, Professor Alan Esker, Katie Farmer, Joe Polidan

POSS = Polyhedral Oligomeric Silsesquioxane



- Traditional silsesquioxane chemistry focused on "T-Resins"
- The maximization of property enhancements in polymers results from interaction at the -level (Edwards AFRL/PRSM —> POSS monomers)

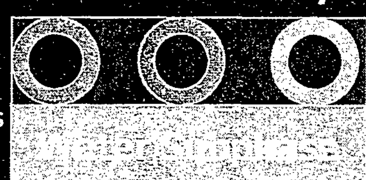
5

What is suppose to be on this slide?

Motivation – Filled Nanofluids

Blends Confined at the Air/Water Interface

Small Sample Requirements



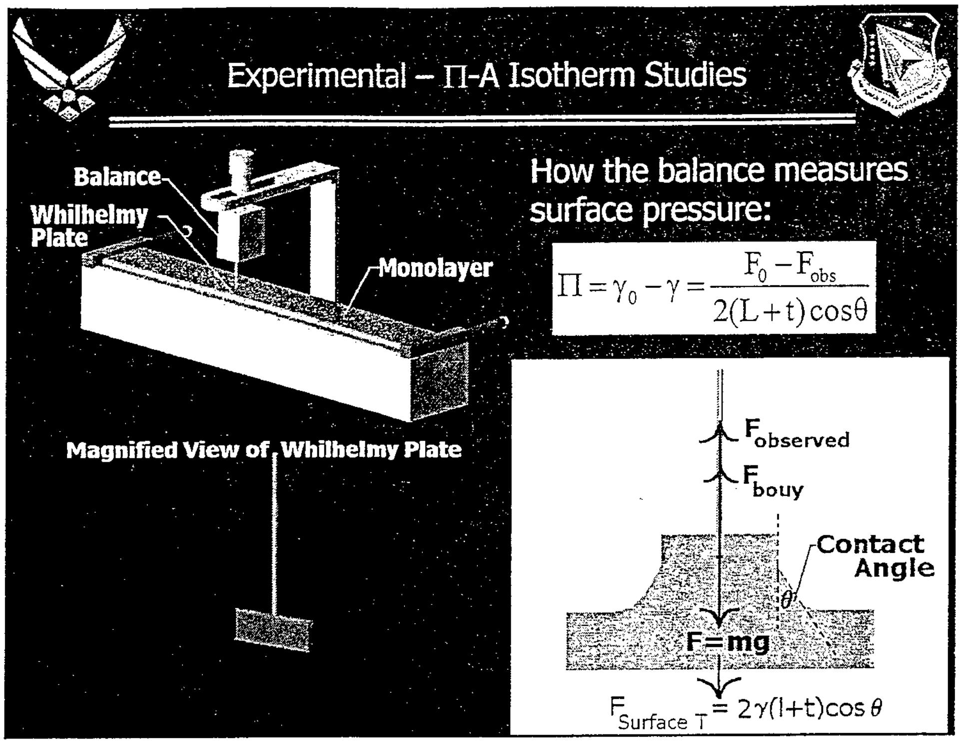
1-2 nm "2-D"

Polymer, Interphase, & Inorganic Core

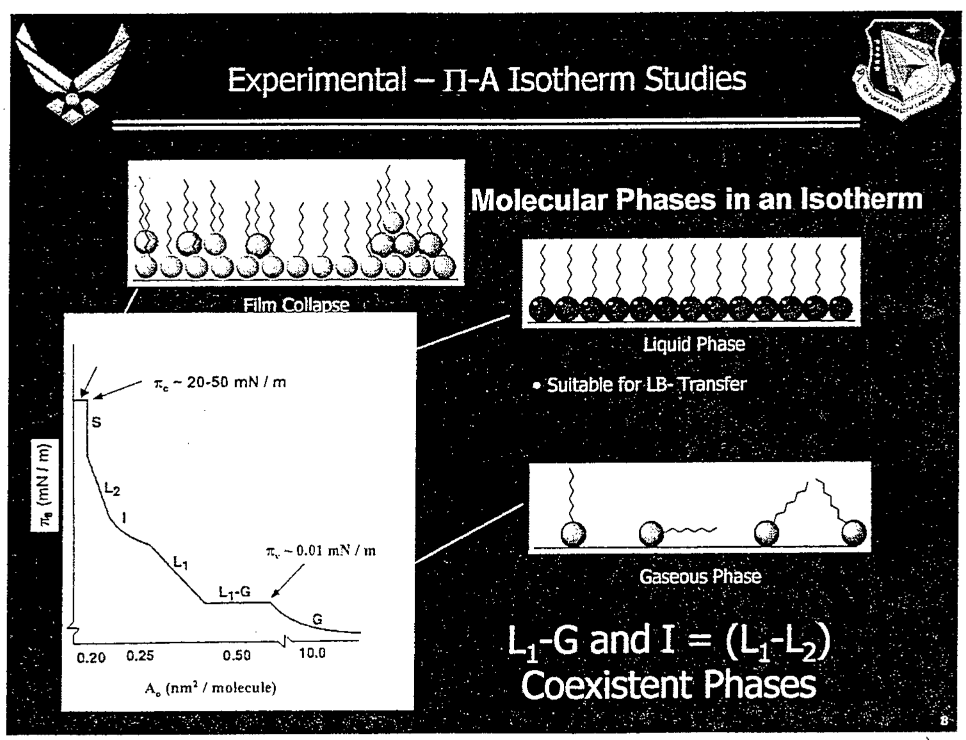
Subphase Affinity is an Important Variable

- A/W poor solvent for PDMS & PtBA ⇒ solvent exclusion
- A/W good solvent for PVAc ⇒ chain swelling (must consider water's contribution)

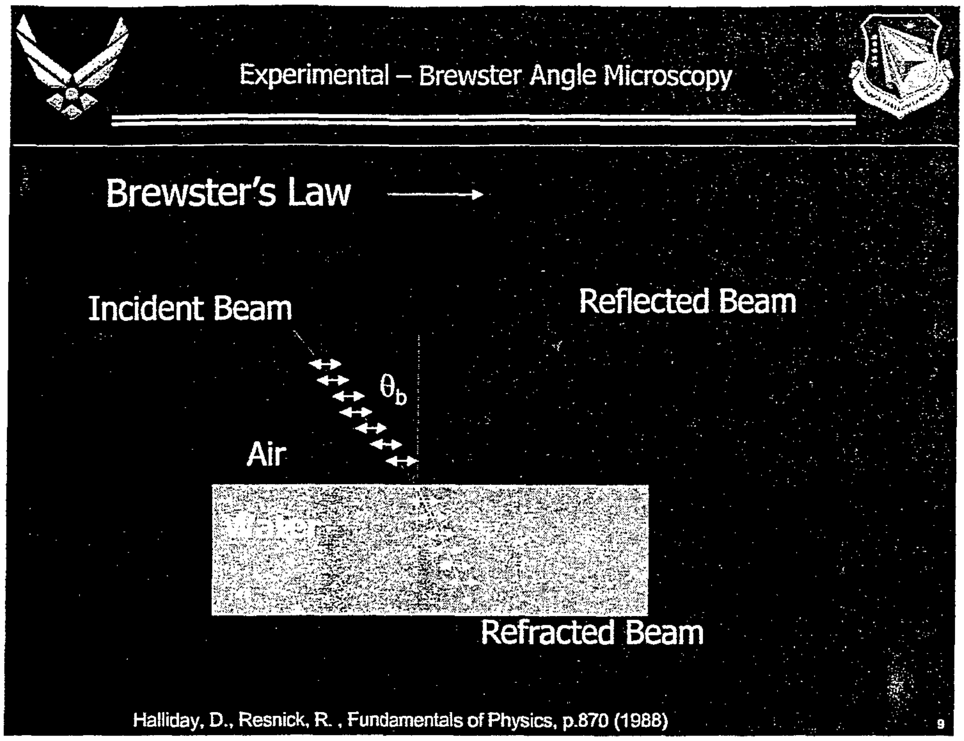
6

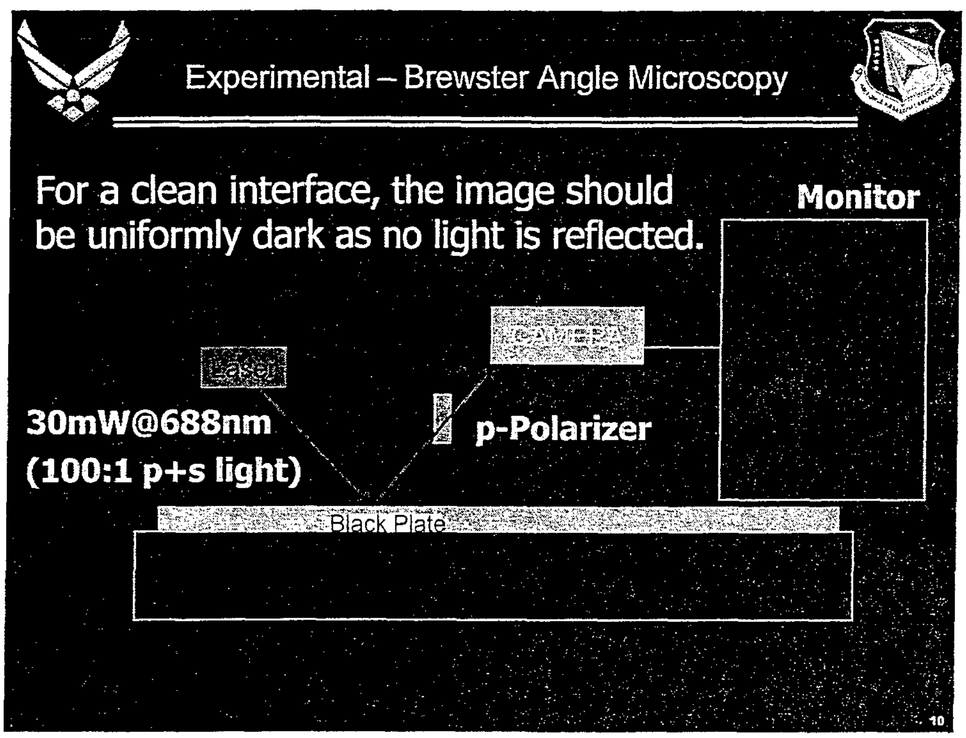


Experimental – Π-A Isotherm Studies
Balance
Whilhelmy Plate
Monolayer
Magnified View of Whilhelmy Plate
How the balance measures surface pressure:
$\Pi = \gamma_0 - \gamma = \frac{F_0 - F_{obs}}{2(L+t)\cos\theta}$
$F_{observed}$
F_{bouy}
Contact Angle
θ
F=mg
$F_{Surface\ T} = 2\gamma(l+t)\cos\theta$



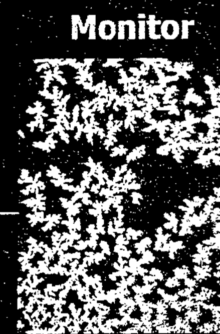
Experimental – Π-A Isotherm Studies
Molecular Phases in an Isotherm
Film Collapse
Liquid Phase
• Suitable for LB- Transfer
Gaseous Phase
π_c ~ 20-50 mN / m
S
L_2
I
L_1
L_1-G
π_v ~ 0.01 mN / m
G
π_s (mN / m)
0.20 0.25 0.50 10.0
A_o (nm^2 / molecule)
L_1-G and I = (L_1-L_2) Coexistent Phases
8

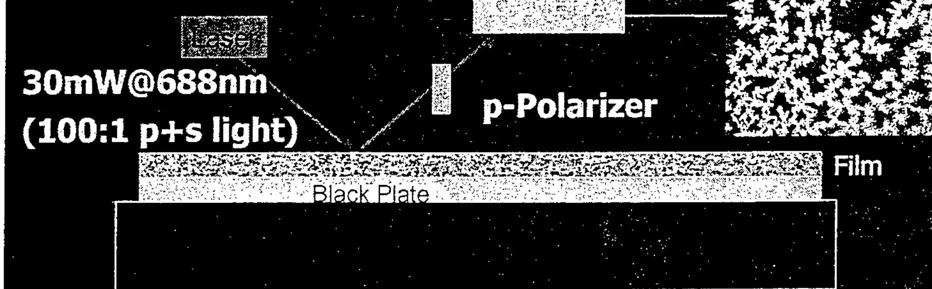

Experimental – Brewster Angle Microscopy
Brewster's Law
Incident Beam
Reflected Beam
θb
Air
Refracted Beam
Halliday, D., Resnick, R. , Fundamentals of Physics, p.870 (1988)
9


Experimental – Brewster Angle Microscopy
For a clean interface, the image should be uniformly dark as no light is reflected.
Monitor
30mW@688nm
(100:1 p+s light)
p-Polarizer
Black Plate
10

Experimental – Brewster Angle Microscopy

Surface heterogeneity (>20μm) is observable by this technique.





Experimental – Systems Studied

Polymers – Structural Models for Adhesive Polymers

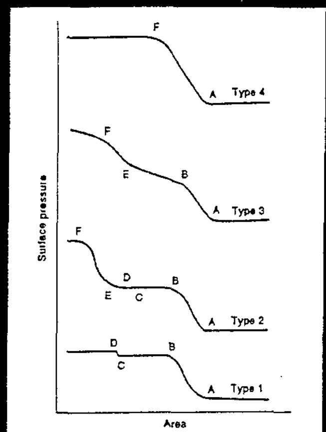
PDMS: $M_n \approx 2k$ PVAc: $M_v \approx 1280k$ **PtBA: $M_n \approx 25k$**

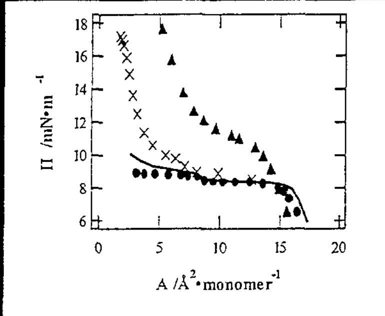
POSS Derivatives

- Octaisobutyl-POSS
- Isobutyltrisilanol-POSS
- Cyclopentyltrisilanol-POSS
- Cyclohexyltrisilanol-POSS

PDMS Langmuir Blodgett Analysis

- **Inherent dimensionality effects**





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× mono COOH; ● di $Si(CH_3)_3$; — di OH

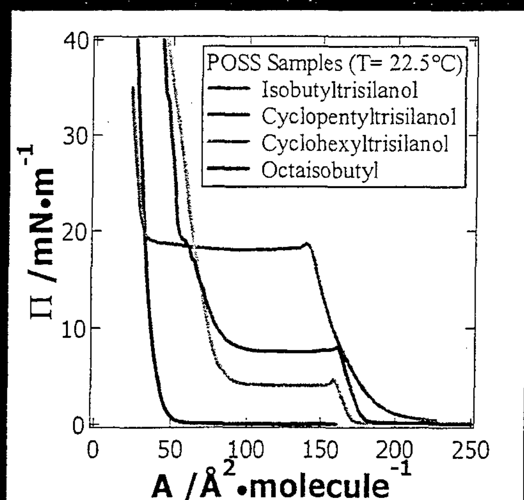
•**Highly sensitive to functionality**

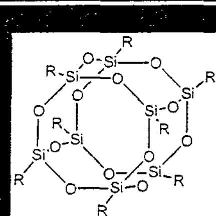
Lenk, Koberstein, et. Al. *Langmuir*, 10, 1857

↑

- "al." should not be capitalized
- Please add a comma after "al." to separate the journal name

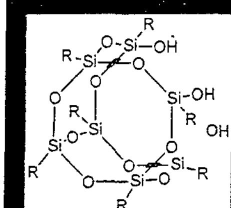
Results – P-A Isotherms of F





R_8T_8

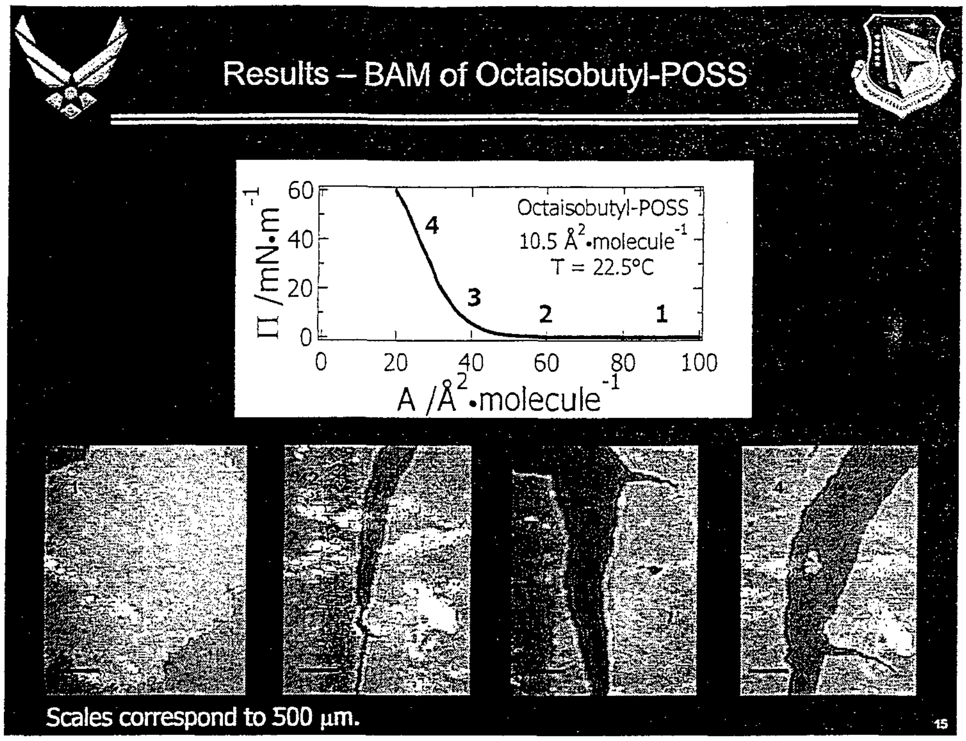
Weak Interactions

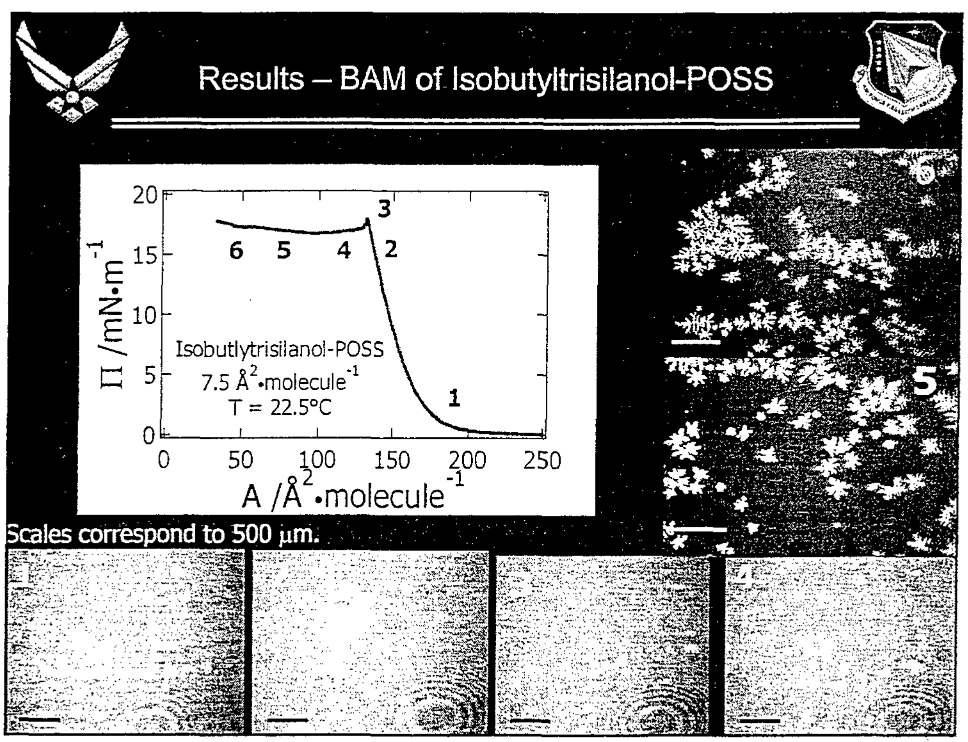


R_7T_7

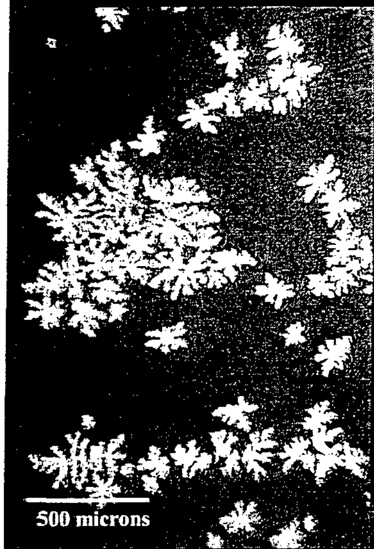
Stronger Interactions

Virginia Tech


Results – BAM of Octaisobutyl-POSS
Octaisobutyl-POSS
10.5 Å²•molecule⁻¹
T = 22.5°C
Π /mN•m⁻¹
A /Å²•molecule⁻¹
0
20
40
60
80
100
1
2
3
4
Scales correspond to 500 μm.
15


Results – BAM of Isobutyltrisilanol-POSS
Isobutlytrisilanol-POSS
7.5 Å²•molecule⁻¹
T = 22.5°C
Π /mN•m⁻¹
A /Å²•molecule⁻¹
0
5
10
15
20
50
100
150
200
250
1
2
3
4
5
6
Scales correspond to 500 μm.

Results – BAM of Isobutyltrisilanol-POSS



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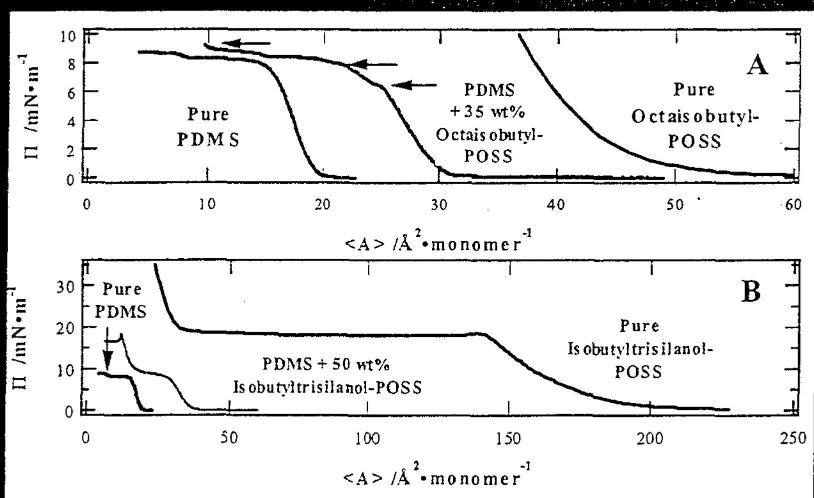
- Pressure relaxation drives the system to the equilibrium state characterized by round domains
- Observed in a few other surfactant systems*

*Iimora,K.-I.;*et al.* *Langmuir* **2001**, *17*, 4602

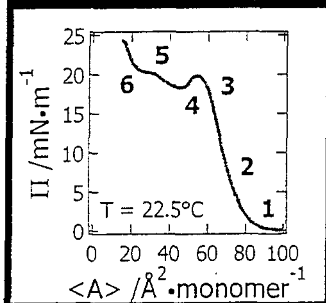
I suggest adding a comma here to separate the authors from the journal name

POSS-

$$\Delta G^{*,\sigma} = \int_{\Pi}^{\Pi^*} (A_{12} - x_1 A_1 - x_2 A_2)\, d\Pi$$



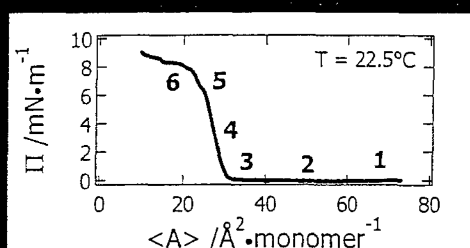
Results – 80 wt% iBu_7T_7/PtBA Blend

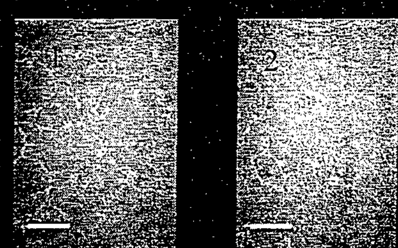


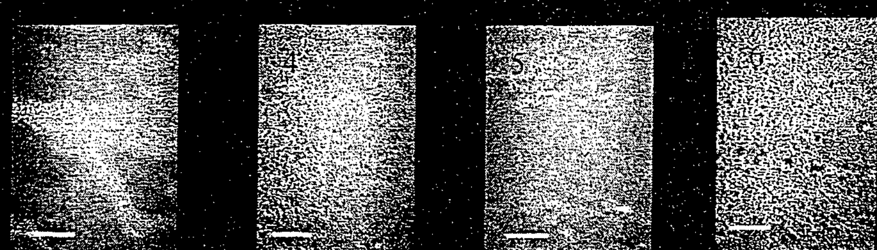
- Ideal uniform blends (0-100 wt%POSS, 1-3), LB<50wt% POSS
- Dendritic domains form at 4 (50-100 wt%) POSS, size ↑ as POSS ↑, round domains (POSS < 50 wt%)
- Banded structure ⇒ PtBA collapse
- 6* = 60 wt% iBu_7T_7/PtBA blend

Scales correspond to 500 µm.

Results – 35wt% Octaisobutyl-POSS/PDMS

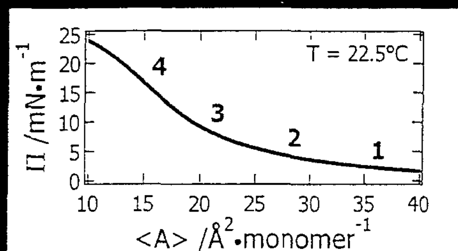




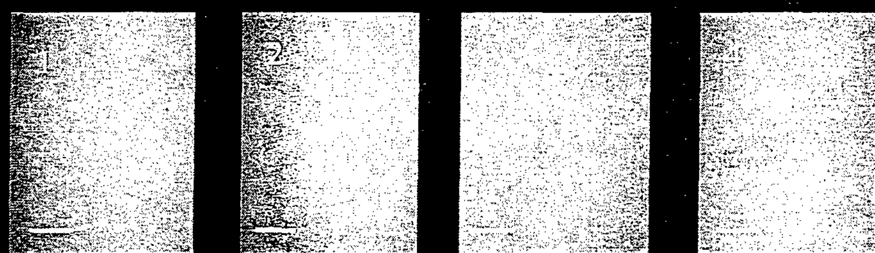


Scales correspond to 500 µm.

Results – 35wt% Octaisobutyl-POSS/PVAc

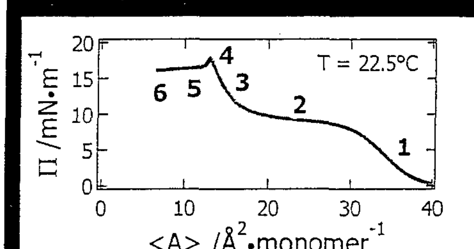


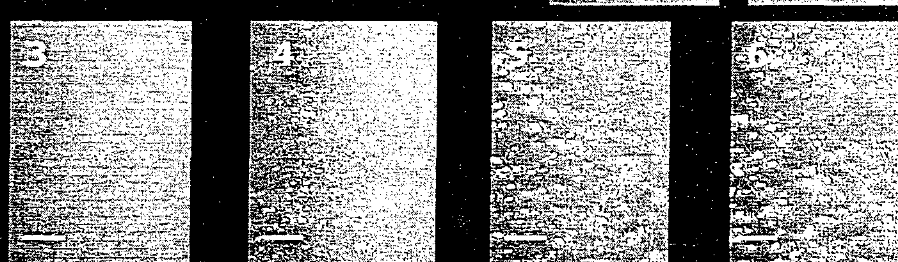
- PVAc/iBu_8T_8: Non-ideal mixing like PDMS/iBu_8T_8
- Unlike PDMS system, POSS is almost completely excluded from the interface!!!



Scales correspond to 500 μm.

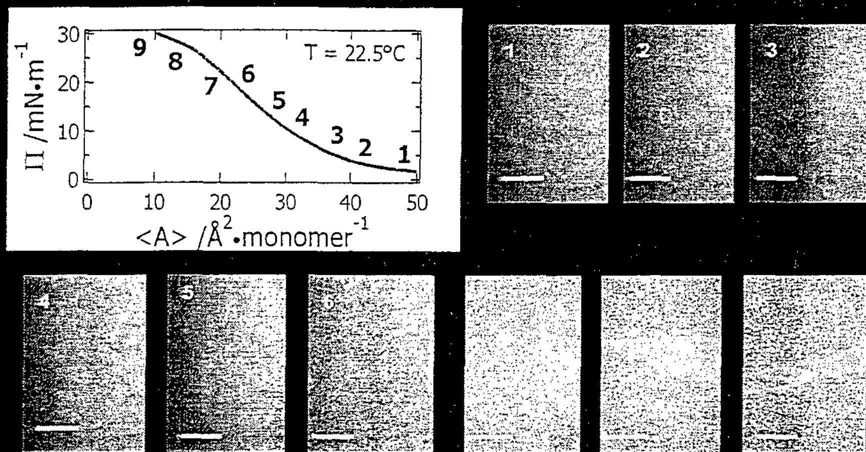
Results – 50wt% Isobutyltrisilanol-POSS/PDMS





Scales correspond to 500 μm.

Results – 50wt% Isobutyltrisilanol-POSS/PVAc



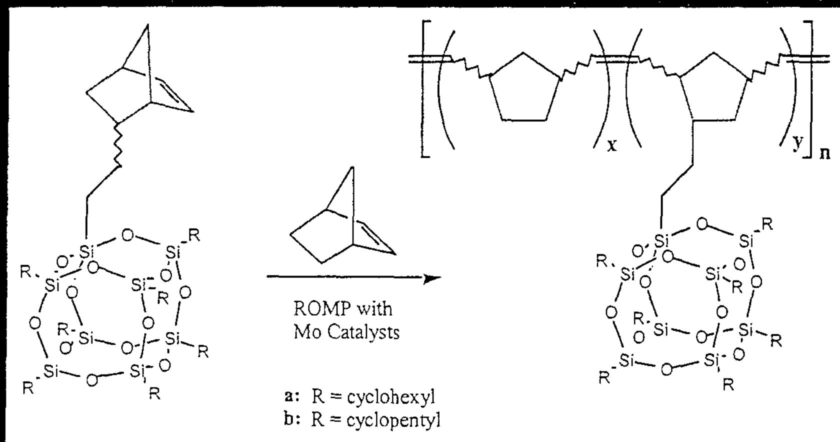
Scales correspond to 500 μm.

Summary: POSS Blends

- POSS derivatives exhibit surfactant properties that vary with structure
- Homogeneous films with near ideal mixing for iBu_7T_7+PDMS, PVAc or PtBA (P < 18 mN•m^{-1}), but BAM shows samples are dispersions
- For P > 18 mN•m^{-1}, non-equilibrium dendritic domains form for pure iBu_7T_7 & iBu_7T_7+PtBA (>50wt% POSS), round domains as POSS
- I Bu_7T_7+PDMS uniform dispersions (>mm), iBu_7T_7+PVAc immiscible (>mm)

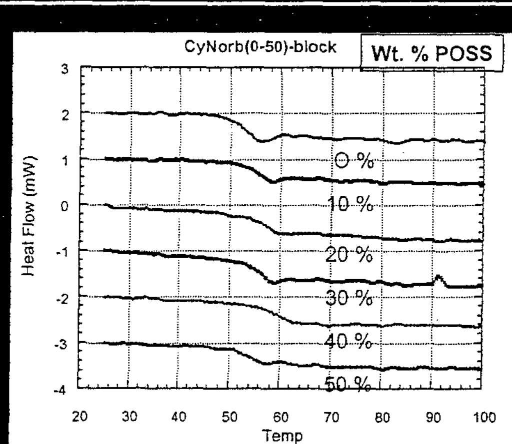
Virginia Tech

Model POSS Polymers- POSS Norbornene



- Both block and random copolymers were synthesized.
- The amount of POSS was varied from 0 to 60 wt. % POSS.

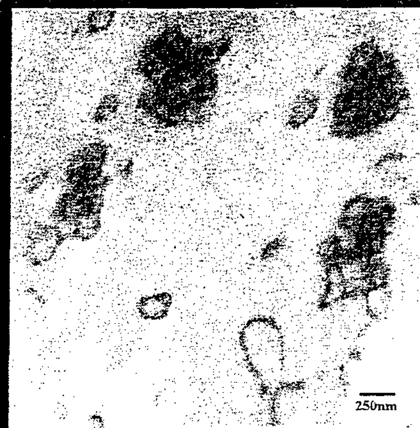
POSS-block-norbornene



- Only a single Tg is observed from the norbornene block.
- The POSS norbornene block does not give rise to any transition up to 350 °C
- Homo polymers of POSS-styryls and acrylates show the same behavior.

Morphology of POSS/PN Diblock Copolymers (TEM)

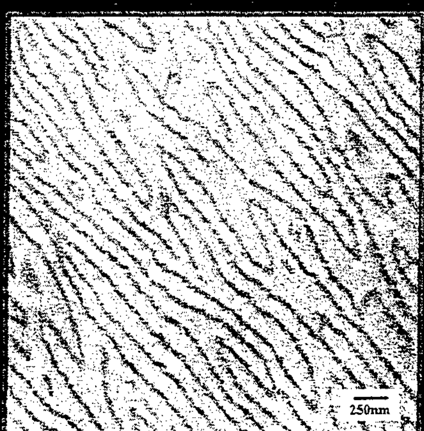
10wt% of CyPOSS



10wt % of CpPOSS

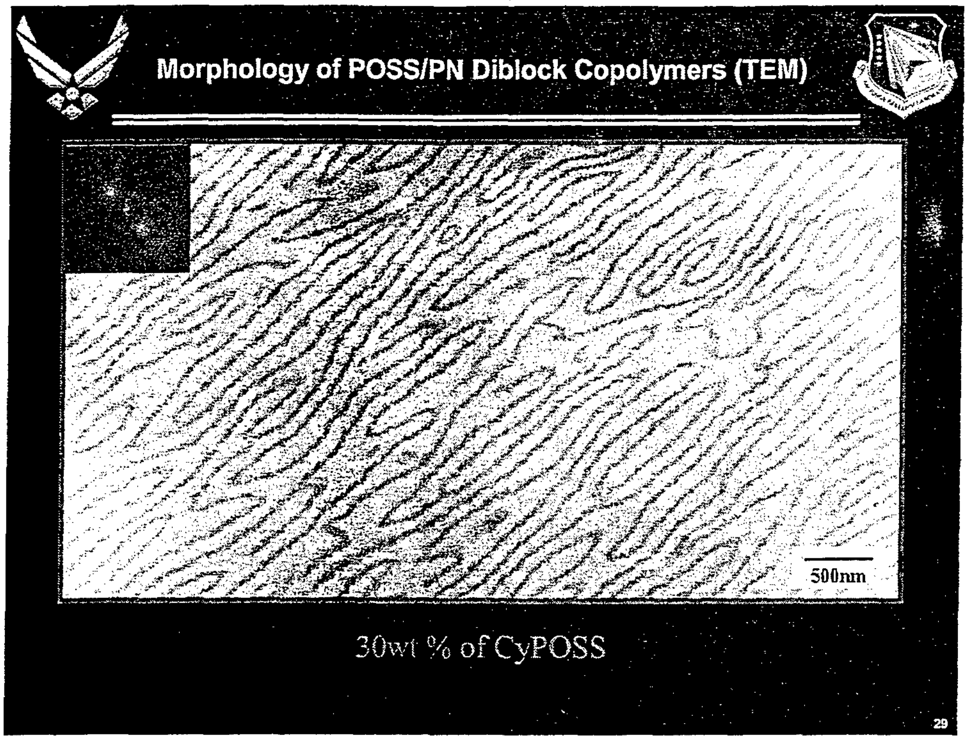
- CyPOSS is more soluble in the polymer matrix than CpPOSS
- Also seen for random polymers, resulting in a greater ΔT_g for CyPOSS

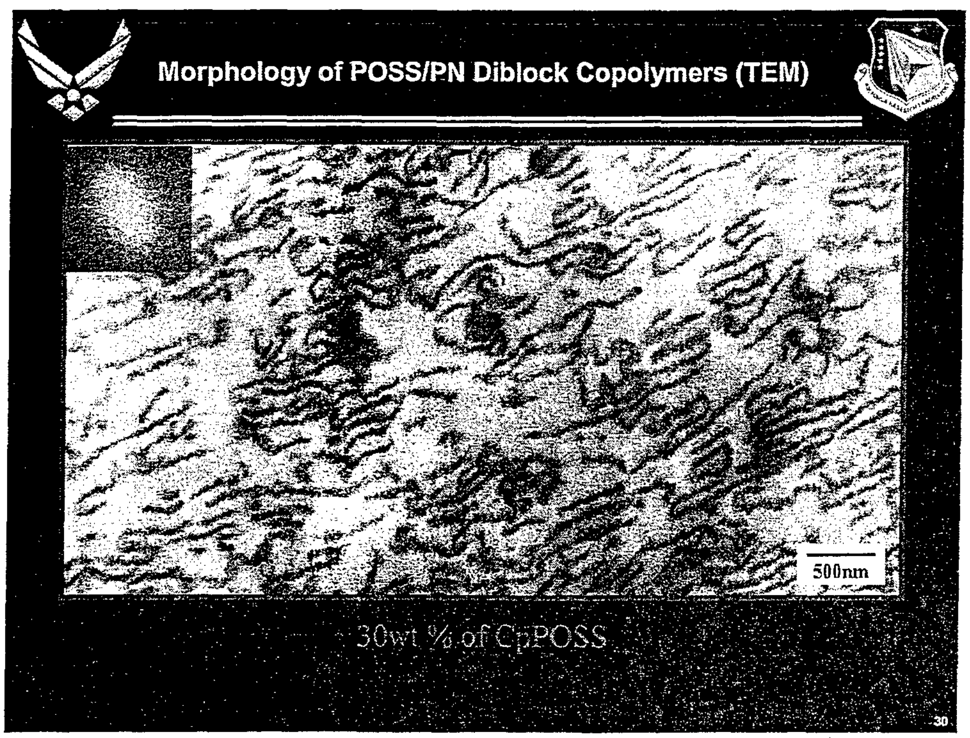
Morphology of POSS/PN Diblock Copolymers (TEM)



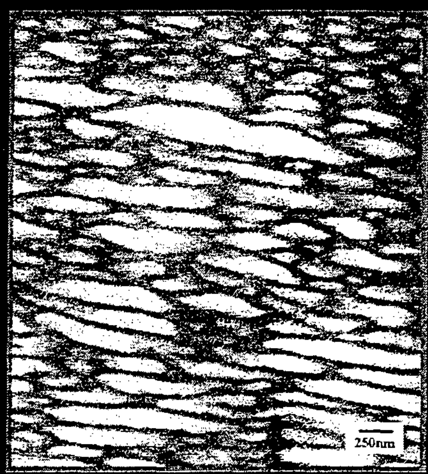
30wt % of CyPOSS

30wt% of CpPOSS


Morphology of POSS/PN Diblock Copolymers (TEM)
500nm
30wt % of CyPOSS
29


Morphology of POSS/PN Diblock Copolymers (TEM)
500nm
30wt % of CpPOSS
30

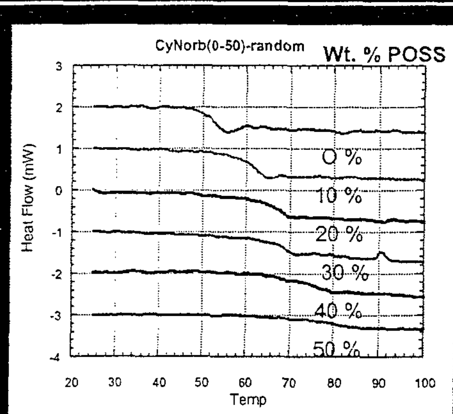
Morphology of POSS/PN Diblock Copolymers (TEM)



60wt% of CyPOSS

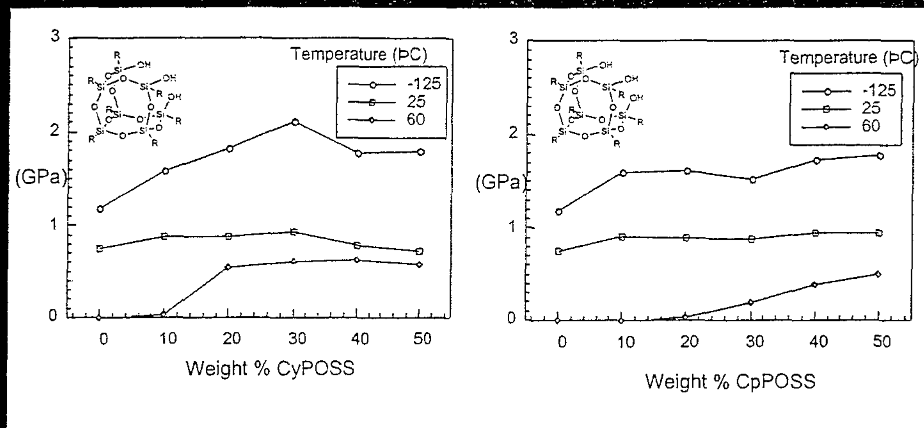
60wt% of CpPOSS

DSC Data for Random Copolymers



- Random copolymerization: Material with a single Tg is obtained that increases with increasing POSS content
- Effect stronger than that observed for POSS-styryl, but not as large as for POSS-acrylics.

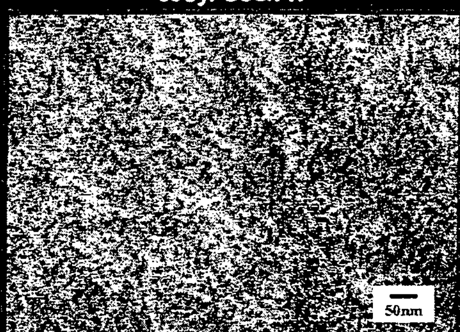
Tensile Storage Modulus Variation with POSS Content at Three Temperatures



Up to 50 weight % of POSS-nobornene was incorporated into the norbornene copolymer without adversely affecting the room temperature modulus, and increasing the use temperature of these materials over 50 °C.

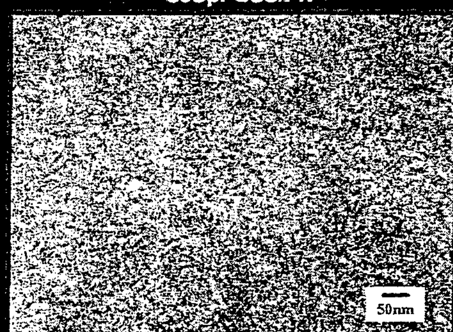
TEM of 50CpPOSS/PN & 50CyPOSS/PN

50CyPOSS/PN



"Coarse" Cylinder Nanostructure
(Diameter ~ 12nm)

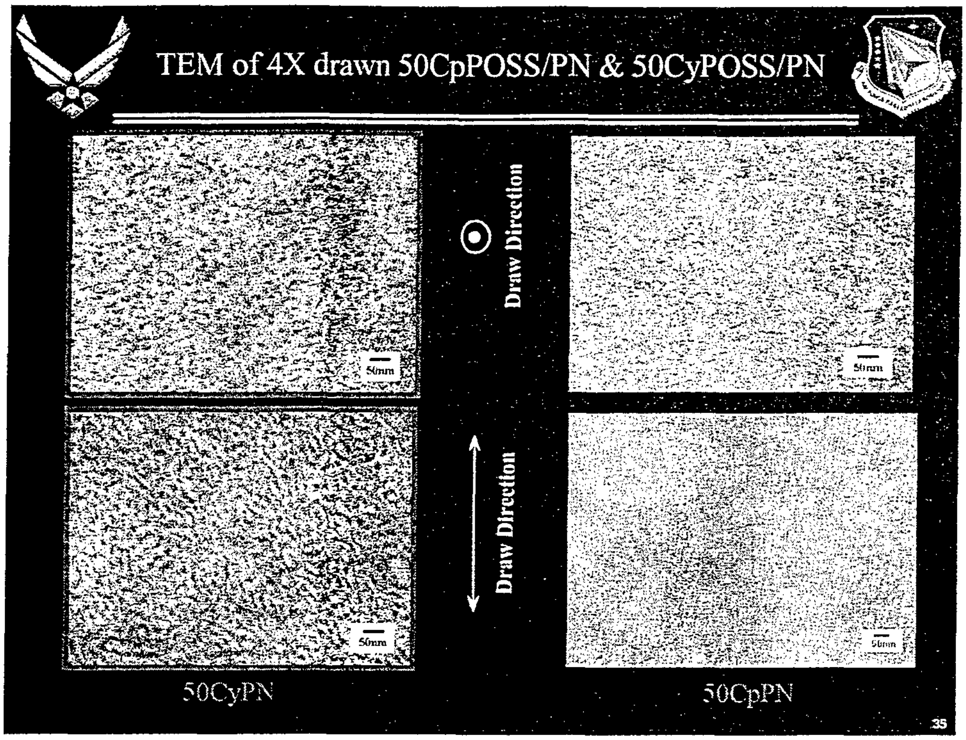
50CpPOSS/PN

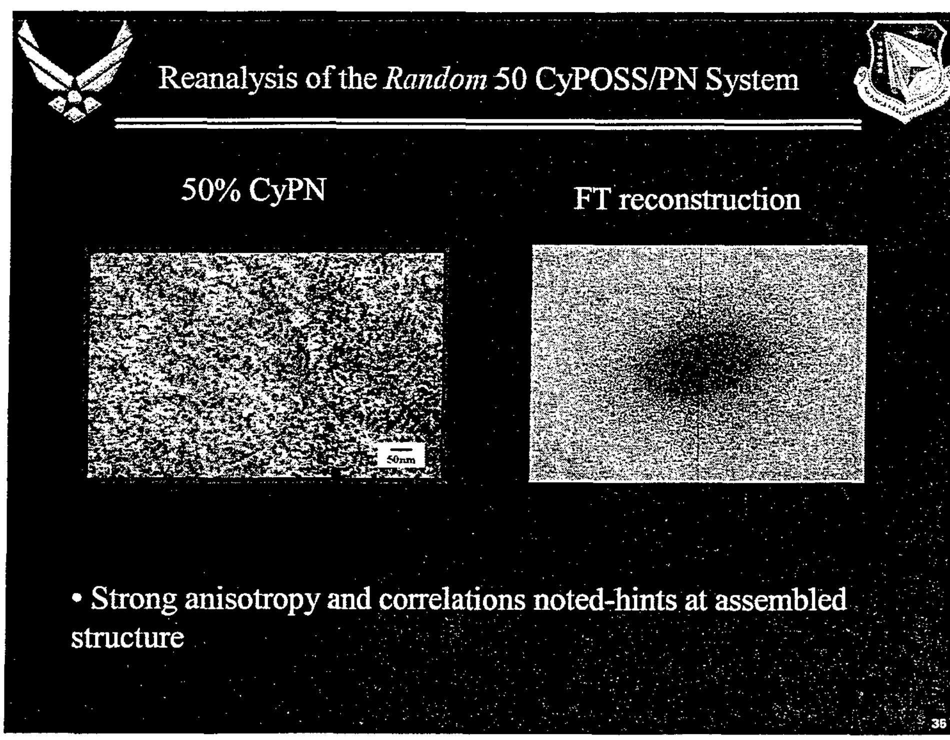


"Fine" Cylinder Nanodstructure
(Diameter ~ 6nm)

← Nanostructure ?

CyPOSS-rich domains may entrain more unoriented PN chains than CpPOSS-rich domains, which could reduce the recoverable strain.

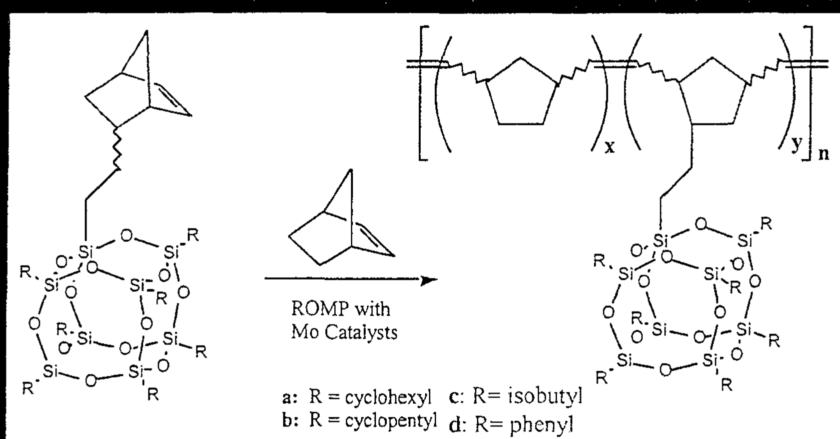

TEM of 4X drawn 50CpPOSS/PN & 50CyPOSS/PN
Draw Direction
Draw Direction
50nm
50nm
50nm
50nm
50CyPN
50CpPN
35


Reanalysis of the *Random* 50 CyPOSS/PN System
50% CyPN
FT reconstruction
50nm
• Strong anisotropy and correlations noted-hints at assembled structure
36

Summary: POSS copolymers

- A variety of POSS "monomers" can be copolymerized into common systems (styrenic, acrylics, polyimides, etc.)
- The polymierzation parameters don't appear to be greatly affected, and the POSS is compatible with the matrix (optically transparent)
- The model POSS-norbornene copolymers show distinct differences in mechanical behavior and morphology for differences in POSS corona chemistry (cyclopentyl vs. cyclohexyl)
- Evidence of larger scale structures.

Variations on the theme-POSS corona chemistry



- Differing POSS corona polynorbornenes being synthesized

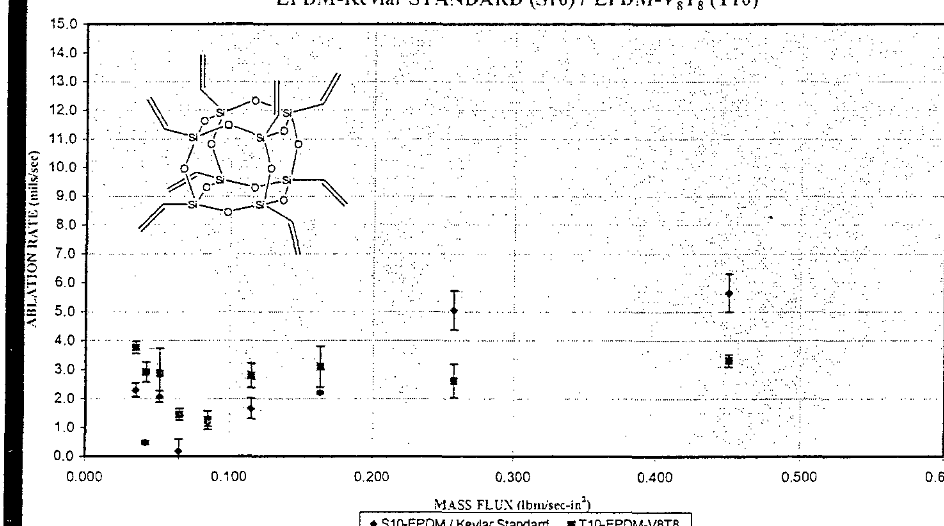
Polymeric Materials for Aerospace

- Offer many advantages
  - Lightweight
  - Easy to process
  - Versatility
  - Optically transparent or opaque
  - Rubbery or stiff
  - Conductive or insulating
- However, their use is limited due to severe degradation in operation (Low Earth Orbit, high speed, high flux)

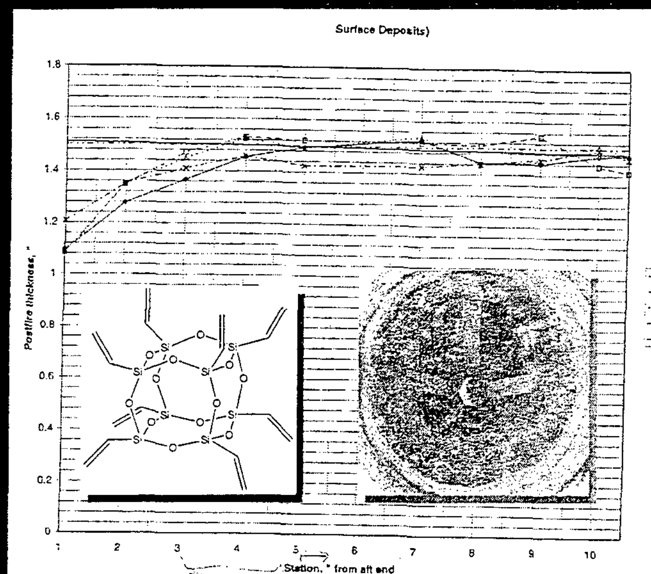
POSS Reinforcement-Pi-K motor

CHAR-063 ABLATION RATE

EPDM-Kevlar STANDARD (S10) / EPDM-V_8T_8 (T10)

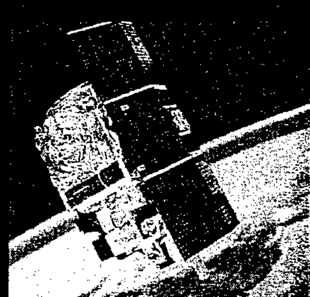


POSS Reinforcement-CSD tests



- 40-lb ITM Motor
- A series of POSS/EPDMs were tested
- Most promising was Vi8T8

Goal: Develop Multi-Functional, Space-Resistant Materials

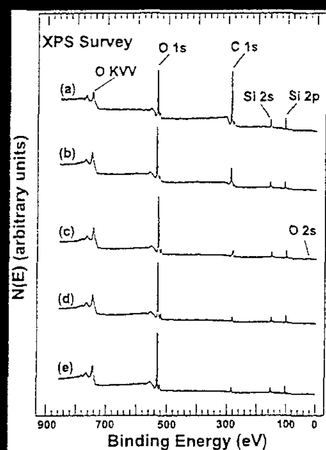


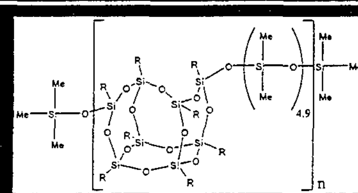
Bond	Dissociation Energy (EV)	λ (nm)	Material
$-C_6H_4-C(=O)-$	3.9	320	Kapton®
C-N	3.2	390	Kapton®
CF_3-CF_3	4.3	290	FEP Teflon®
CF_2-F	5.5	230	FEP Teflon®
Si-O	8.3	150	Nanocomposite
Zr-O	8.1	150	Nanocomposite
Al-O	5.3	230	Nanocomposite

Objectives

- Increase Space Resistance (AO, particle & VUV radiation, thermal cycling) of Polymeric Materials
- Self-Passivating/Self-Rigidizing/Self-Healing based on organic/ inorganic nanocomposite incorporation

Atomic Oxygen Resistance of POSS Siloxane

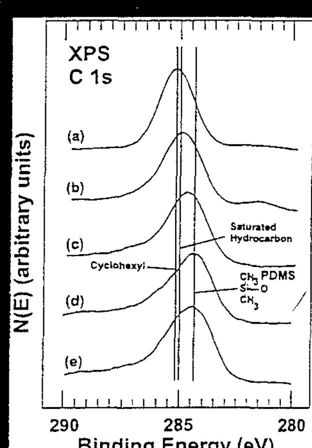


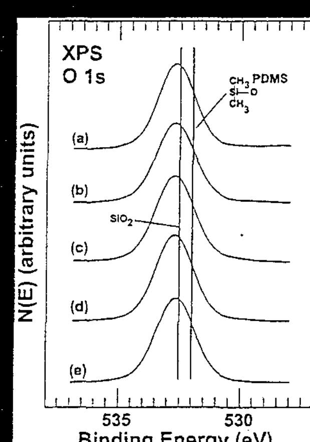


Sample Treatment	O	C	Si
As entered	18.5	65.0	16.6
2.0 hr	33.8	48.4	17.8
24.6 hr	49.1	22.1	28.8
63.0 hr	55.7	16.3	28.0
4.8 hr air	52.8	19.5	27.7

XPS survey spectra obtained from a solvent-cleaned, POSS-PDMS film (a) after insertion into the vacuum system, (b), after a 2-hr (c) 24.6-hr and (d) 63-hr exposure to the hyperthermal AO flux, and (e) 4.75-hr air exposure following the 63-hr AO exposure.

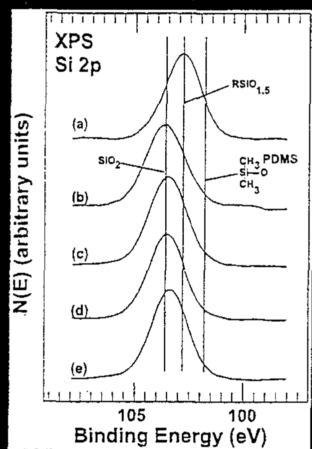
Atomic Oxygen Resistance of POSS Siloxane





High Resolution C 1s and O 1s spectra obtained from a solvent-cleaned, POSS-PDMS film (a) after insertion into the vacuum system, (b), after a 2-hr (c) 24.6-hr and (d) 63-hr exposure to the hyperthermal AO flux, and (e) 4.75-hr air exposure following the 63-hr AO exposure.

Atomic Oxygen Resistance of POSS Siloxane



High Resolution Si 2p spectra obtained from a solvent-cleaned, POSS-PDMS film (a) after insertion into the vacuum system, (b), after a 2-hr (c) 24.6-hr and (d) 63-hr exposure to the hyperthermal AO flux, and (e) 4.75-hr air exposure following the 63-hr AO exposure.

Summary: Aerospace Polymers

- POSS can be compatabilized into traditional systems in high loadings (>50 wt%), allowing great opportunity for ceramic formation
- The reactive POSS corona, or the incompletely oxidized silsesquioxane core might favor the formation of the protective ceramic coating